

Radiation Effects in Glasses for Intrinsic Optical Fibre Radiation Dosimetry

by

Christopher A. G. Kalnins

A thesis submitted in fulfillment of the degree of Doctor of Philosophy

in the

Faculty of Sciences School of Chemistry and Physics University of Adelaide, Australia

August 2015

Abstract

An optical fibre device has been developed for the purpose of detecting ionising radiation using optically stimulated luminescence. Characterisation of glass materials has been performed, after which optical fibres were fabricated for experiments to demonstrate sensing of ionising radiation.

Fluoride phosphate glass was tested for its capability to sense ionising radiation, primarily using the mechanism of optically stimulated luminescence. The characteristics of the material were determined using a combination of spectroscopy, and thermally and optically stimulated luminescence tests. The sensitivity to ionising radiation was improved by introducing dopant ions into the glass; doping of fluoride phosphate glass with Tb³⁺ was found to increase the intensity of the optically stimulated luminescence response by an order of magnitude, from 7.56×10^6 counts/g/Gy to 100.7×10^6 counts/g/Gy.

Optical fibres were fabricated from fluoride phosphate glass using the extrusion method for fibre preform manufacture. The fabrication process was optimised in each of the extrusion, preform processing and fibre drawing stages to achieve optical fibres with loss of between 0.5 - 1 dB/m for undoped fibres, and between 1 - 4 dB/m for Tb³⁺doped fibres. Optical fibres were used for ionising radiation sensing experiments, where the optically stimulated luminescence response was measured following both beta and X-ray irradiation. Following a dose of 14.6 ± 0.5 Gy, optically stimulated luminescence signals were observable using optical fibre lengths of up to 2.6 m, with an integrated OSL intensity of 44.1 ± 13.0 counts.

Silica glass was also tested as an alternative material to perform optical fibre measurements using optically stimulated luminescence. The material was characterised and optical fibres were fabricated with a loss of 0.5 dB/m. Following a dose of 15.5 ± 0.5 Gy, optically stimulated luminescence signals were observable using optical fibre lengths of up to 8.6 m, with an integrated OSL intensity of 385.7 ± 43.4 counts.

Declaration

I, Christopher A. G. Kalnins, declare that this thesis titled 'Radiation Effects in Glasses for Intrinsic Optical Fibre Radiation Dosimetry' and the work presented in it are my own.

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

I give consent to this copy of my thesis, when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library Search and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

Signed

Date

Acknowledgements

Firstly I would like to thank my supervisors: Heike Ebendorff-Heidepriem, Nigel Spooner and Tanya Monro. Your patience and guidance through each stage of this work has been invaluable and without it, this thesis would not exist.

For their technical support, I wish to thank Alastair Dowler, Herbert Foo, Kevin Kuan, Rachel Moore, Kenton Knight, Peter Henry and Donald Creighton. Your assistance with fibre drawing, glass and preform fabrication, and 3D thermoluminescence spectrometry has been invaluable.

The Institute for Photonics and Advanced Sensing and The School of Chemistry and Physics have been instrumental in creating a fantastic working environment, both professionally and socially. In particular I would like to express my pleasure to have worked within the Environmental Luminescence, Chemical and Radiation Sensing, and Fabrication groups.

For their financial support and usage of equipment and facilities, I would like to thank the Defence Science and Technology Organisation. For usage of fabrication facilities, the South Australian node of the Australian National Fabrication Facility is also acknowledged.

On a personal note, I would like to extend my gratitude to my family who have supported and encouraged me not just through this thesis, but through my whole life. Mum, Dad and Nici, you've been an inspiring family to grow up in.

For bringing not only fun and warmth, but also a strong feeling of belief and encouragement, my gratitude goes out to Antonija. Thank you for being by my side.

For their dark and bitter humour, without which I could not have seen the bigger picture of life, I must thank all my friends. I appreciate every single one of you and what you bring into my life. Many of you are also pursuing research degrees, and I have enjoyed the solidarity as we question our life choices.

Lastly and perhaps most importantly, I would like to acknowledge EDM, chocolate and the peace found at 2 am.

Contents

A	bstra	\mathbf{ct}		i
D	eclar	ation		i
A	cknov	wledge	ements	ii
Ta	able o	of Con	itents	iii
Sι	ımma	ary		ix
T.i	st of	Figur	05	vi
	50 01	rigui		Л
Li	st of	Table	s	xxiii
1	Intr	oduct	ion	1
	1.1	Introd	luction to Radiation Dosimetry	2
		1.1.1	History of Dosimetry	. 2
		1.1.2	Examples of Dosimetry	. 2
	1.2	State-	of-the-Art of Optical Fibre-Based Radiation Sensing	. 4
		1.2.1	Radioluminescence	5
		1.2.2	Photodarkening	6
		1.2.3	Thermoluminescence	6
		1.2.4	Bragg Gratings	. 7
		1.2.5	Optically Stimulated Luminescence	. 7
		1.2.6	Comparison of Extrinsic and Intrinsic Sensing Methods	. 8
		1.2.7	Advantages of Fibre-Based Sensing	. 9
	1.3	Lumir	nescence Theory	. 10
		1.3.1	Optically Stimulated Luminescence	10
		1.3.2	Thermoluminescence	. 14
	1.4	Dose 1	Deposition Within Materials	16
		1.4.1	Photon Interactions	. 18
		1.4.2	Electron and Positron Interactions	. 18

		1.4.3	Radiation Sources	19
	1.5	Simula	ation of Energy Deposition	22
		1.5.1	Motivation	22
		1.5.2	Simulation Package and Theory (PENELOPE)	22
		1.5.3	Physical Processes Simulated by PENELOPE	23
		1.5.4	Abilities and limitations	23
	1.6	Projec	t Constraints and Opportunities	24
		1.6.1	Glass Fabrication Facilities	24
		1.6.2	Detection Systems	24
	1.7	Compa	arison of Detectors	25
	1.8	Thesis	Overview	26
2	Ide	ntificat	ion and Characterisation of Fluoride Phosphate Glass	30
	2.1	Initial	Survey of Glass Characteristics	31
		2.1.1	Glass Samples	31
		2.1.2	Screening for Optically Stimulated Luminescence	31
	2.2	Fluori	de-phosphate Glass	33
		2.2.1	Varieties of Fluoride Phosphate Samples	33
	2.3	Comp	osition	34
		2.3.1	Electron Microprobe	34
		2.3.2	ICP-MS/OES	36
	2.4	Transr	nission Spectra and Photodarkening	36
		2.4.1	Effect of Photodarkening	37
		2.4.2	Emission Spectra	40
	2.5	Redox	State of Fluoride Phosphate Glass	41
	2.6	Lumin	escence Characterisation of Fluoride Phosphate Glass	41
		2.6.1	Thermoluminescence Measurements	42
		2.6.2	Optically stimulated luminescence	46
	2.7	Simula	ations of Radiation Penetration and Dose Deposition	53
		2.7.1	Stopping Power	54
		2.7.2	Energy Transfer	54
		2.7.3	Range of Electrons	56
		2.7.4	Dose Deposition Profiles	57
	2.8	Summ	ary	58
3	Fab	ricatio	n and Characterisation of Doped Fluoride Phosphate glass	60
	3.1	Choice	e of Dopant Ions	61
	3.2	Fabric	ation of Doped Fluoride Phosphate Glasses	61
		3.2.1	Oxidising Atmosphere	62

		3.2.2	Reducing Atmosphere	62
		3.2.3	Sample Summary	63
	3.3	Spectr	$\operatorname{roscopy}$	63
		3.3.1	Copper	64
		3.3.2	Manganese	64
		3.3.3	$Terbium \dots \dots$	64
		3.3.4	Radioluminescence Spectra	67
	3.4	Optica	ally and Thermally Stimulated Luminescence Measurements θ	68
		3.4.1	Copper	71
		3.4.2	Manganese	73
		3.4.3	Terbium	76
		3.4.4	Summary	81
	3.5	Anom	alous Fading	83
		3.5.1	Theory	83
		3.5.2	Experiment to Detect and Observe Anomalous Fading 8	83
		3.5.3	Results	85
	3.6	Summ	nary of Dopant Properties	86
4	Fab	ricatio	on of Fluoride Phosphate Optical Fibres	88
	4.1	Introd	luction	89
		4.1.1	State-of-the-Art	89
		4.1.2	Glass Material	89
		4.1.3	Fibre Geometry	89
	4.2	Extru	sion	90
		4.2.1	Die Materials	91
		4.2.2	Extrusion Force, Speed and Temperature	91
		4.2.3	Limit on Extrusion Temperature	93
		4.2.4	Atmosphere	94
	4.3	Prefor	rm Treatment	94
		4.3.1	Energy Dispersive X-ray Spectroscopy	94
		4.3.2	Optical Profiling	95
		4.3.3	Chemical Etching	96
		4.3.4	Mechanical Polishing	98
	4.4	Fibre	Fabrication)1
		4.4.1	Fibre Characterisation)1
		4.4.2	Fibre Drawing)1
	4.5	Summ	ary of Optical Fibre Quality)3
	4.6	Doped	l Fluoride Phosphate Optical Fibres)5
	4.7	Fibre	Jacketing)8

	4.8	Summ	nary
5	Det	ection	of Optically Stimulated Luminescence in Optical Fibres 113
	5.1	Dose 1	Deposition and Radiation Considerations
		5.1.1	Radiation Safety
		5.1.2	Dose Deposition Profiles
		5.1.3	Calculation of Dose Deposition in Fibres
	5.2	Detect	tors, Optical Stimulation and Filters
		5.2.1	Detection with a PMT
		5.2.2	Detection with a SPAD
		5.2.3	Luminescence in the 350 - 600 nm region $\ldots \ldots \ldots \ldots \ldots \ldots \ldots 123$
	5.3	Develo	opment of an Experimental Test-Bed
		5.3.1	Differences Between Bulk and Fibre Measurements
		5.3.2	Signal Detection and Integration
		5.3.3	Improvements in Signal-to-Noise Ratio
		5.3.4	Optical Alignment
	5.4	OSL N	Measurements
		5.4.1	Stimulation Power
		5.4.2	OSL with respect to dose
		5.4.3	Minimum Fibre Size and Mass
		5.4.4	Summary
	5.5	OSL N	Measurements on Tb^{3+} -Doped Optical Fibres
		5.5.1	OSL Tests on Tb^{3+} -Doped Fibre Melted in Reducing Atmosphere 142
		5.5.2	OSL Tests on Tb^{3+} -Doped Fibre Melted in Oxidising Atmosphere 144
		5.5.3	Summary
	5.6	Detect	tion of X-rays
		5.6.1	Experimental Setup
		5.6.2	Results
	5.7	Summ	nary
6	Inve	estigat	ion of the Radiation-Detecting properties of Silica Optical
	Fib	res	159
	6.1	Introd	luction $\ldots \ldots \ldots$
	6.2	Silica	Glass Samples
		6.2.1	Fluorescence Emission
	6.3	Thern	nally and Optically Stimulated Luminescence
		Measu	rements
		6.3.1	Optically Stimulated Luminescence
		6.3.2	Thermoluminescence

		6.3.3	Thermoluminescence Emission Spectrometry 165	
		6.3.4	Initial Rise Thermoluminescence	
	6.4	OSL in	a Silica Fibres and Canes	
		6.4.1	Fabrication of Silica Fibres and Canes	
		6.4.2	OSL in Optical Fibres	
		6.4.3	Dose Dependence	
		6.4.4	X-ray Irradiation	
	6.5	Compa	arison of Silica and Fluoride Phosphate Glasses	
		6.5.1	Transmission Loss	
		6.5.2	Mechanical Strength and Jacketing	
		6.5.3	Thermal Properties	
		6.5.4	Trap Lifetime	
		6.5.5	Doping of Glasses	
		6.5.6	Luminescence	
		6.5.7	Bleaching and Re-usability	
	6.6	Conclu	sions $\ldots \ldots 184$	
7	Disc	cussion	. Conclusions and Future Work 185	
•	7.1	Summ	arv of Experimental Work and Kev Results	
	7.2	Trap I	ifetime of Fluoride Phosphate Glass	
	7.3	Feasib	lity of the Optical Fibre Sensor	
	7.4	With 1	Respect to the State of the Art	
	7.5	Altern	ative Ideas for Optical Fibre Dosimetry	
	7.6	Future	Directions	
	7.7	Conclu	usions	
\mathbf{A}	ppen	dices	212	
\mathbf{A}	Mat	terials	and Materials Properties 213	
	A.1	Initial	Glass Screening	
	A.2	Fluorie	de Phosphate Glasses	
		A.2.1	Summary of FP Glass Samples	
		A.2.2	Schott N-FK51A Fluoride Phosphate Glass \hdots	
	A.3	ICPM	S/OES Detection Limits $\dots \dots \dots$	
	A.4	Silica	Glass	
	A.5	Fluorio	de Phosphate Glass Radiation Interaction Values	
в	Inst	rumen	tation and Fabrication Facilities 226	
_	B.1	Risø T	L/OSL DA-20 Reader	
		B.1.1	Sample Preparation	
			· · · · · · · · · · · · · · · · · · ·	

		B.1.2 Sample Irradiation	27
		B.1.3 Luminescence Detection	27
	B.2	Glass Fabrication	28
	B.3	Extrusion Machine	28
	B.4	Fibre Draw Tower	30
С	Fab	rication Data 2	34
U	I ab.		01
	C.1	Extrusion Data	34
	C.2	Fibre Drawing Data	34
D	PE	NELOPE Simulations 23	36
	D.1	Stopping Power Calculations	36
	D.2	Electron and Photon Absorption in FP Glass	36
	D.3	Examples of Simulation Input Files	39

Summary

This thesis contains a study of the feasibility of detecting ionising radiation with an optical fibre, specifically using the mechanism of optically stimulated luminescence. This work addresses the particular case where the radiation sensing occurs within the optical fibre material, and not in a separate material otherwise spliced to a fibre. The optical fibre therefore acts as both the sensing component of the device, and the wave-guiding component which carries a signal to the detector. This work fills a void in the already-established range of optical fibre dosimetry technologies, and provides an alternative method for performing optical fibre dosimetry.

To achieve the project goals, glass materials were studied for their optical, luminescence and radiation detecting properties. These glasses were then fabricated into optical fibres, and these fibres tested in a variety of radiation environments. Work was initially performed with fluoride phosphate glasses, where the glass was characterised and then altered by the addition of various dopant ions to improve its radiation detecting sensitivity. Silica glasses were later studied as a comparison to fluoride phosphate glasses. Also presented is the fabrication of these glass materials into optical fibres of suitable quality to perform distributed sensing measurements of ionising radiation. The performance of the optical fibres are studied under both beta and X-ray irradiation conditions, and their usefulness as dosimeter devices is assessed.

Chapter 1 outlines the context and motivation behind the presented work, and provides a short introduction to the theory behind the experimental work. Chapter 2 explores the various properties of the materials used for optical fibre fabrication, primarily focusing on fluoride phosphate glasses. In Chapter 3, the modification of fluoride phosphate glasses with dopant ions in order to improve the sensitivity as a radiation detecting material is presented. Chapter 4 presents the fabrication of the radiation sensitive material into optical fibres of sufficient mechanical strength and optical quality for radiation sensing experiments. The radiation sensing experiments for which these optical fibres were used are shown in Chapter 5. Chapter 6 presents an alternative material, silica, and shows how in some areas it can be superior to the materials discussed in previous chapters. Chapter 7 summarises the experimental work and gives an appraisal on the feasibility of using this novel method of radiation sensing in real-world applications; this is followed by a summary of future directions for this area of research.

List of Figures

1.1	Extrinsic (top) and intrinsic (bottom) optical fibre architectures. Red	
	indicates the region over which the radiation sensing phosphor is active.	8
1.2	Mechanism of optically stimulated luminescence, showing 1) dose deposi-	
	tion 2) electron trapping and 3) stimulation and recombination. Ionising	
	radiation is shown in red, optical stimulation in green and stimulated lu-	
	minescence emission in blue	10
1.3	(1) Ionising radiation deposits energy. (2) Luminescence is emitted in	
	4π (blue), only a fraction is captured by the guided modes of the fibre	
	(darker blue). (3) This captured luminescence is guided in each direction	
	down the fibre.	12
1.4	Integrated area of OSL signal	13
1.5	Mechanism of thermoluminescence, showing 1) dose deposition 2) elec-	
	tron trapping and 3) thermal stimulation and recombination. Ionising	
	radiation is shown in red, thermal stimulation by a campfire and the	
	stimulated luminescence in blue.	15
1.6	Glow peaks of a thermoluminescence 'glow curve', showing where data	
	may be integrated to analyse a given peak. Red lines indicate the region	
	used for 'initial rise' TL measurements. The sharp rising feature at	
	higher temperature is a depiction of the incandescence signal	16
1.7	Electron (top) and photon (bottom) showers in silicon dioxide, each for	
	$2.28~{\rm MeV}$ primary energy. Data was simulated using PENELOPE, the	
	process of which is explained in Section 1.5. \ldots \ldots \ldots \ldots \ldots	17
1.8	Interactions of photons with matter.	19
1.9	Interaction of electrons with matter	20
1.10	Representation of a typical bremsstrahlung spectrum. Table inset lists	
	the energies of the ${\rm K}_{\alpha}$ and ${\rm K}_{\beta}$ characteristic X-ray peaks for tungsten	21
1.11	Quantum efficiency of a PMT (EMI 9235 QB) compared with two single $$	
	photon avalanche diodes, Micro Photon Devices (MPD) and Lasercom-	
	ponents (COUNT®-blue).	27

1.12	Overview of experimental process from the initial glass analysis through to radiation sensing measurements with optical fibres. Blue lines: chrono- logical timeline of experiments. Red lines: experimental results used to	
	guide analysis and fabrication of new materials and fibres	29
2.1 2.2	Example of an OSL response from a variety of the glass samples examined. Composition of fluoride phosphate glasses as determined by an electron microprobe. Data was taken from multiple points on the glass surface for each sample	32
2.3	Transmission spectra of several different samples of FP glass, taken using	00
	1 mm thick polished slides	38
2.4	Photodarkening in Schott N-FK51A fluoride phosphate glass over 7 hours $$	
	due to irradiation with a 90 Sr/ 90 Y Beta source	39
2.5	Annealing of colour centers by heat treatment at 200 $^{\circ}\!\mathrm{C}$ for 2 hours	39
2.6	Emission spectra of several FP glass samples	40
2.7	Thermoluminescence of FP1 glass melted in different redox conditions	43
2.8	Initial rise thermoluminescence for Schott N-FK51A fluoride phosphate	
	glass	44
2.9	Calculation of the slope for $ln(I)$ vs. $1/T$, from which values for E , s	
	and τ are extracted	44
2.10	Thermoluminescence emission spectrum of undoped FP1 glass. Top = $% \left[\left({{{\left[{{\left[{\left[{\left[{\left[{\left[{\left[{\left[{\left[$	
	ambient melting conditions, bottom = reducing melting conditions	46
2.11	Complete bleaching of FP1 and FP1 red glass in both the 275 - 400	
	nm and 350 - 600 nm wavebands, using 470 nm and 870 nm optical $$	
	stimulation respectively. Results are given for different bleaching times	
	between measurements, 5 s and 30 s, the optical power incident on each	
	sample is shown in the legend. Lines are provided only as a guide for	
	the eye	50
2.12	OSL signal of fluoride phosphate glass as a function of the applied dosage.	
	Trendlines indicate a linear response from 0 - 2 Gy, and an exponential	
	response from 2 - 30 Gy	51
2.13	(a) $ln(I/I_0)$ vs. t and (b) $(I/I_0)^{(1-b)/b}$ vs. t. Data shown is for measure-	
	ments taken at ambient temperature on FP1 glass	52
2.14	OSL with respect to the stimulation power of the diode arrays in the	
	Risø Reader.	53
2.15	Stopping power of fluoride phosphate glass over a range of particle energies.	54
2.16	Simulated energy absorbed from a 2.28 MeV electron beam (left) and a	
	100 keV photon beam (right) by layers of FP glass with varying thickness.	55

2.17	Simulated energy of transmitted primary particles from a 2.28 MeV elec- tron beam (left) and a 100 keV photon beam (right) by layers of FP glass	
2.18	with varying thickness. Simulation was performed using PENELOPE Dose deposition profile of a parallel electron beam into fluoride phosphate	56
2.10	glass	58
2.19	Dose deposition profile of a parallel photon beam into fluoride phosphate glass	59
3.1	Emission spectra of sample Cu-red-60 under a reducing environment,	
	copper concentration is 60 ppmwt	65
3.2	Absorption spectra of FP1 glass doped with copper ions and melted	
	under ambient and reducing atmospheres	65
3.3	Emission spectra of FP1 glass doped with manganese. \ldots	66
3.4	Absorption spectra of FP1 glass doped with manganese and melted under $% \mathcal{A}$	
	ambient and reducing atmospheres	66
3.5	Emission spectra of sample Tb-red. Excitation at 355 nm with a mercury	
	lamp and a frequency tripled YAG laser	67
3.6	Absorption spectra of FP1 glass doped with Tb^{3+} and melted under	
	ambient and reducing atmospheres	69
3.7	Experimental setup for measuring the spectra of RL from bulk glass	
	samples	69
3.8	RL spectra of Schott N-FK51A fluoride phosphate glass. Excitation with	
	a 320 MBq 90 Sr/ 90 Y beta source, described in Section 5.1.	70
3.9	TL spectra of fluoride phosphate glasses doped with copper under am-	
	bient and reducing atmospheres	71
3.10	Thermoluminescence emission spectrum of sample Cu-red, 3D and in-	
	tensity contour plots	72
3.11	OSL shine-down trace for copper doped FP glass compared with undoped	
	glass, produced under both oxidising and reducing conditions. Copper	
	concentration is 60 ppmwt for each doped sample. Above: OSL detected	
	using 470 nm optical stimulation and a HOYA U340 filter. Bottom: OSL	
	detected using 870 nm optical stimulation and a Schott BG39 filter. $\ .$.	74
3.12	Integrated OSL counts from FP1 glass doped with Cu^+ under a reducing	
	environment. Lines are included only as a guide for the eye	75
3.13	TL emission of Mn^{2+} doped FP glass	75
3.14	Thermoluminescence emission spectrum of sample Mn-ox, shown as both	
	3D and intensity-contour plots to highlight the dominance of 600 nm	
	Mn^{2+} emission	76

3.15	OSL shine-down trace for manganese doped FP glass compared with	
	undoped glass, produced under both oxidising and reducing conditions.	
	Manganese concentration is 2749 ppmwt for each doped sample. Above:	
	OSL detected using 470 nm optical stimulation and a HOYA U340 filter.	
	Bottom: OSL detected using 870 nm optical stimulation and a Schott	
	BG39 filter	77
3.16	TL emission of Tb^{3+} -doped FP glass	78
3.17	Thermoluminescence emission spectrum of sample Tb - red, 3D and	
	intensity contour plots. The series of peaks seen for fluorescence and	
	scintillation measurements are also clearly visible in the 400 – 600 nm $$	
	region	79
3.18	OSL shine-down trace for terbium doped FP glass compared with un-	
	doped glass, produced under both oxidising and reducing conditions.	
	Terbium concentration is 7200 ppmwt for each doped sample. Above:	
	OSL detected using 470 nm optical stimulation and a HOYA U340 filter.	
	Bottom: OSL detected using 870 nm optical stimulation and a Schott	
	BG39 filter	80
3.19	Reproducibility of sample Tb-ox glass with different 'bleaching' periods	
	between individual OSL measurements. One set of measurements is	
	taken using 5 s (167.2 mJ) of optical stimulation at 870 nm and the	
	other with 100 s (1672 mJ). Measurements were taken using a Schott	
	BG39 filter. Lines are included only as a guide for the eye	81
3.20	Plot of the OSL data provided in Table 3.4, shown for both $275 - 400$ and	
	$350-600~\mathrm{nm}$ wavelength regions. Results shown for samples fabricated	
	under both oxidising and reducing conditions	82
3.21	Anomalous fading of undoped and doped FP glasses following a one hour	
	pause after irradiation	84
3.22	Luminescence from sample Mn-ox, following irradiation and pre-heat	
	to 230 °C. Sample receives no stimulation during data collection; the	
	sample was held at ambient temperature for this measurement	86
3.23	Emission spectra of Mn^{2+} and Tb^{3+} -doped FP1 glass compared with	
	the transmission spectrum for a 3 mm thick Schott BG39 filter	87
4.1	Cross-section of the extrusion process. This diagram shows only the	
	inner section of the setup, surrounding the body is a furnace, which is	
	controlled using feedback from the thermocouple. The puncher enters	
	through the top of the furnace, and the extruded preform exists through	
	the bottom.	90

4.2	Preform surface quality following extrusion through Macor (\mathbb{R}) at 525 °C
	at speeds of (left) 0.2 mm/min and (right) 0.1 mm/min
4.3	Effect on FP1 glass of heating to 525 $^{\circ}\mathrm{C}$ in a furnace. Left: unheated
	sample of FP1 glass, right: FP1 glass following heating to 525 °C 94
4.4	Composition of optical fibre preform surface compared with the bulk
	material, measured using the scanning electron microscope on EDX mode. 95
4.5	Examples of surface defects taken using the Optical Profiler using VSI
	mode. Note the colour-coded height scales can change significantly,
	based on the scale of the surface measured
4.6	Etching efficiency of fluoride phosphate glass by 0.6 M AlCl_3 in 1M HCl,
	etching efficiency in mg/min is calculated from the slope
4.7	Surface profile of a fluoride phosphate preform showing (a) unetched and
	(b) etched surfaces
4.8	Surface of preform throughout the polishing process. Time = (a) $0 \min$
	(b) 10 min (c) 30 min (d) 90 min
4.9	Surface roughness with respect to the polishing time of an FP preform
	surface with colloidal silica. Lines are included only as a guide for the eye 100
4.10	Comparison of neckdown region between (a) unpolished and (b) polished
	preforms. All other fabrication conditions were constant 104
4.11	Neckdown region of fluoride phosphate fibre preform remains imaged
	with an optical profiler. The surface layer has been drawn into a corru-
	gated structure. The fibre drawing direction is in line with the corruga-
	tions and toward the bottom of the figure
4.12	Loss in undoped fluoride phosphate optical fibres 105
4.13	Loss of selected undoped FP1 optical fibres at 550 nm. Polishing of fibre
	preforms was commenced for fibre trial F11. Due to high loss or fibre
	pull failure, not every fibre trial result can be shown. In two cases (F12 $$
	and F13)) preforms were drawn down into canes, not fibres, hence no
	loss result is shown
4.14	Loss of fluoride phosphate optical fibres fabricated from polished pre-
	forms extruded through Macor \textcircled{R} and stainless steel 106
4.15	$\rm Tb^{3+}\text{-}doped$ FP glass billet, polished in preparation for extrusion. $\rm Tb^{3+}\text{-}$
	concentration is 7200 ppmwt, billet mass is 102.6 g 109

4.16	Comparison of loss in undoped and Tb^{3+} -doped fluoride phosphate op- tical fibres. Optical fibres were fabricated from glasses melted in both oxidising and reducing atmospheric conditions. F15: Undoped, F17:
	Tb ³⁺ -doped 7200 ppmwt reducing atmosphere, F18: Tb ³⁺ -doped 720 ppmwt reducing atmosphere F19: Tb ³⁺ -doped 7200 ppmwt oxidising
	atmosphere
4.17	Crystalline and bubble defects in Tb^{3+} -doped FP preform (E17). Sev-
	approximately 5 - 10 mm
4 18	Absorbed energy comparison of (a) 2.28 MeV beta particles and (b) 2.28
1.10	MeV photons within a 160 μ m thick slab of FP glass with PVC layers
	of varying thickness
5.1	Dose comparison in a 160 μm thick slab of FP glass with and without
	an aluminium backing
5.2	TL Calibration curve of dose delivered to a 7.5 mm $\rm Tb^{3+}\text{-}doped$ FP1
	fibre section
5.3	Transmission spectra of dichroic filters used for isolation of the lumi-
	nescence signal from the optical stimulation. Note that for the 800 nm
	dichroic, the stimulation laser is reflected and the luminescence signal is
	transmitted through to the detector; for the 505 nm dichroic, the stimu-
	lation laser is transmitted and the luminescence signal is reflected toward
	the detector. $\ldots \ldots 120$
5.4	Transmission spectra of individual coloured glass filters used in the $\operatorname{Ris} \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \!$
	Reader and for OSL tests on the experimental test-bed. The Schott BG3 $$
	filter is 3 mm thick, the Hoya U340 is 7.5 mm thick, the Corning 7-59 $$
	is a stack of 3 mm and 4 mm filters totalling 7 mm in thickness, the
	necessary thickness to adequately suppress scattered photons at 532 nm.
	For suppression of scattered photons at $852~\mathrm{nm},$ a BG39 filter 3mm thick
	is sufficient
5.5	Output spectra of the lasers used for OSL measurements in optical fibres. 122
5.6	Transmission spectra of the individual coloured glass (3 mm thick) and
	interference filters used for OSL measurements
5.7	Suppression of the 700 - 1100 nm transmission window with composite
	filters. Composite filters are constructed by stacking a BG39 filter with
	$700~{\rm and}~800~{\rm nm}$ short pass interference filters, and also separately with
	a Schott BG39 filter. The Schott BG3 and BG39 filters are both 3 mm
	thick

5.8	Experimental setup for the detection of OSL from a coiled fibre bun-
	dle with a PMT, the optical stimulation at 532 nm is shown in green,
	luminescence is shown in violet
5.9	OSL response from bundles of 160 µm diameter FP optical fibres, in-
	creasing the number of fibres in the bundle increases the OSL intensity.
	No observable OSL was measured from a single fibre at this stage. The
	shutter for optical stimulation was operated manually, hence OSL is ob-
	served at slightly different times from the onset of data acquisition. Lines
	are included only to assist in distinguishing the data
5.10	OSL signal from a fibre bundle. Each measurement is taken with a
	different number of total fibres in the bundle
5.11	Isolation of the detector from scattered photons decreases the back-
	ground noise; scattered photons are due to both ambient light sources
	and the laser optical stimulation. In addition, performing experiments
	in black-out conditions reduces the background further. Data was taken
	from two different optical fibres, therefore light sums should not be di-
	rectly compared, the data serves as a demonstration of background counts.131
5.12	RL and OSL signals from a bundle of FP1 optical fibres, each of which
	are marked on the plot. Irradiation is from a ${}^{90}\mathrm{Sr}/{}^{90}\mathrm{Y}$ beta source,
	optical stimulation at 532 nm, detection with an EMI 9635 QA PMT $$
	using a 4 mm Corning 7-59 filter
5.13	Sample holder designed to hold an optical fibre coiled in a near light-
	tight environment underneath a $^{90}\mathrm{Sr}/^{90}\mathrm{Y}$ beta source. It is machined
	from a luminium in order to provide a material with low Z number for
	conversion of beta particles into low-energy bremsstrahlung emission.
	Red lines indicate the position of a fibre in the holder without the cover
	plate (left), and the holder is also shown with its cover plate and the
	beta source in position (right)
5.14	Schematic representation of the set-up for a fibre bundle and a cane 134
5.15	Experimental setup for the detection of OSL from glass canes using a
	PMT. The optical stimulation at 532 nm is shown in green, luminescence
	is shown in violet, the 405 nm laser used to assist optical alignment is
	shown in blue
5.16	OSL response from a 1 mm FP cane compared with a bundle of 32, 160 $$
	µm diameter FP fibres. In order to compare the results here, data has
	been normalised for the bin time of data collection: a 100 ms bin time
	was used for the bundle, 1 ms was used for the cane
517	Alignment control of fibre output onto the 50 µm SPAD detector chin 136

5.18	OSL in FP glass with respect to stimulation laser power at 532 nm. $$.	138
5.19	OSL response of FP1 glass cane with respect to ${ m ^{90}Sr/^{90}Y}$ exposure time.	139
5.20	OSL response of FP1 glass cane with respect to activity of the ${}^{90}\mathrm{Sr}/{}^{90}\mathrm{Y}$	
	beta source	139
5.21	OSL response of canes with respect to diameter. Dose was approximately	
	14.5 ± 0.5 Gy	141
5.22	Experimental setup for the detection of OSL from a single optical fibre	
	using a SPAD.	141
5.23	Experimental setup for the detection of OSL from glass canes using a	
	SPAD. Optical stimulation at 852 nm is shown in red, luminescence is	
	shown in teal, the 532 nm laser used to assist optical alignment of the	
	system is shown in green.	143
5.24	OSL response of Tb^{3+} -doped fibres/canes with respect to diameter. De-	
	tection was by a SPAD optically filtered by a 3 mm Schott BG39 filter.	
	Dose was approximately 14.6 ± 0.5 Gy	143
5.25	Normalised OSL measurements with respect to the position of the $^{90}\mathrm{Sr}/^{90}\mathrm{Y}$	
	radiation source along glass canes measured from the cane output, cane	
	diameter is 1000 $\mu mu.$ Measurements were taken in the 350 – 600 nm	
	wavelength region using a Schott BG39 filter and optical stimulation at	
	852 nm	144
5.26	Experimental setup for the detection of OSL from a single optical fibre	
	using a SPAD.	145
5.27	Normalised OSL measurements with respect to the position of the $^{90}\mathrm{Sr}/^{90}\mathrm{Y}$	
	radiation source along glass canes measured from the fibre output. Mea-	
	surements were taken in the $350-600$ nm wavelength region using a	
	Schott BG39 filter and optical stimulation at 852 nm. \ldots	145
5.28	Experimental setup for the detection of OSL from a single optical fibre	
	using a SPAD	147
5.29	Schematic representation showing the X-ray beam divergence and the	
	position of the fibre coil in the X-ray beam.	149
5.30	Example of a TL calibration curve of dose delivered to an Al_2O_3 :C	
	dosimeter chip in order to calculate an equivalent dose	149
5.31	X-ray Beam profile obtained from placing Al_2O_3 :C dosimeter crystals at	
	certain x, y positions in the X-ray beam. The dose absorbed by each chip	
	is then calculated from the TL intensity, normalised for the TL response	
	of each individual chip	150

5.32	X-ray imaging plate exposed to the X-ray beam in order to visualise the
	beam intensity profile. Beam attenuation is observed on the right hand
	side due to the X-ray Head handle. No significant fluctuation of beam
	intensity is observed in the central area where optical fibres are positioned.151

5.33	Photodarkening of FP fibres during X-ray exposure, shown by the dimin-	
	ishing transmission of 532 nm laser photons through the fibre under irra-	
	diation during the laser illumination. The plot showing cycled exposure	
	clearly demonstrates the scintillation signal detected during irradiation	
	cycles	153
5.34	OSL from 200 µm fibre (F16) as a function of photon beam intensity at	
	100 and 300 kV tube potentials.	154
5.35	OSL response of 160 µm fibres (F16) with respect to X-ray tube potential	
	at a constant beam intensity of 180 mAs.	155
5.36	PENELOPE simulation of absorbed energy as a function of initial photon	
	energy in FP glass.	156
5.37	OSL from 160 um fibre (F16) as a function of X-ray tube potential at	
	a constant beam intensity of 60 mAs. Aluminium cover plate has been	
	replaced with black tape.	157
6.1	Comparison of OSL from high purity (LWQ) and ultra-high purity (F300)	
	silica glasses. Results are taken using two stimulation wavelength and	
	filter combinations: 870 nm stimulation with a Schott BG39 filter, and	
	470 nm stimulation with a HOYA U340 filter	163
6.2	Reproducibility of silica samples LWQ, MCVD1 and MCVD2 glass in	
	the 350 - 600 nm waveband, a Schott BG39 filter and 870 nm optical	
	stimulation. Results are given for different bleaching times between mea-	
	surements, 5 s and 30 s, the optical power incident on each sample is	
	shown by the graph titles. Lines are provided only as a guide for the eye.	164
6.3	Thermoluminescence of silica glass samples. TL from undoped FP glass	
	is also provided for comparison. No filters were used for TL here, in	
	order to reveal total light sums	165
6.4	Thermoluminescence emission spectra of samples LWQ, MCVD1 and	
	MCVD2, 3D and intensity contour plots. ${}^{90}\mathrm{Sr}/{}^{90}\mathrm{Y}$ irradiation time is	
	300 s, and the heating rate was 5 K/s	166
6.5	Initial rise thermoluminescence for LWQ silica. Measurements followed	
	the procedure described previously in Section 2.6.1. Values of T_m given	
	in the legend are in $^{\circ}C$	167

6.6	Comparison of LWQ and FP glass optical fibres. Both undoped (F15)
	and Tb^{3+} -doped (F19) FP fibres are provided. The bare silica fibre fab-
	ricated for this project (LWQ Silica) is compared with the loss of another
	fibre fabricated from the same glass for a different project (LWQ Silica
	WW 10 $\mu\mathrm{m}$). This demonstrates the high loss measured for LWQ Silica,
	at 0.4 - 0.5 dB/m, higher than the expected 0.1 dB/m observed in the
	fibre LWQ Silica WW 10 μ m. The expected H ₂ O peak at approximately
	1400 nm is observed for both silica fibres
6.7	OSL intensity with respect to the position of the ${ m ^{90}Sr/^{90}Y}$ beta radia-
	tion source along LWQ silica cane (top) and fibres (bottom). Lines are
	included only as a guide for the eye
6.8	Dose dependence of OSL from 1 mm diameter LWQ silica cane. Detec-
	tion using a PMT, optical stimulation at 532 nm and filtration with a
	Schott BG3
6.9	Dose dependence of OSL from 1 mm diameter LWQ silica cane. Detec-
	tion using a SPAD, optical stimulation at 852 nm and filtration with a
	Schott BG39
6.10	Dose dependence of OSL from 1 mm diameter LWQ silica cane. Detec-
	tion using a SPAD, optical stimulation at 852 nm and filtration with a
	Schott BG39. Variation in dose is due to the activity of the ${}^{90}\mathrm{Sr}/{}^{90}\mathrm{Y}$
	beta source. Inset: results were also recorded for the RL with respect to
	activity of the 90 Sr/ 90 Y beta source
6.11	OSL response of LWQ silica fibre with respect to beam intensity at tube
	potentials of 100 and 300 kV
6.12	OSL response with respect to X-ray tube potential using LWQ silica
	optical fibres of varying diameter. Optical stimulation at 852 nm , using
	a Schott BG39 filter. Lines are included only as a guide for the eye. $~$ 177 $$
6.13	Simulation showing energy absorbed (dose) by silica fibre with respect
	to X-ray photon energy
6.14	OSL response with respect to X-ray tube potential at a beam intensity
	of 600 mAs. Measurements taken without the aluminium lid of the fibre
	holder
6.15	(a) OSL response with respect to thickness of aluminium shielding be-
	tween the X-ray source and the fibre. (b) Simulation of absorbed energy
	in an FP glass volume behind aluminium layers of varying thickness us-
	ing PENELOPE. Several different initial photon energies were simulated. 179

6.16	Plot of the OSL data provided in Table 6.7, shown for both $275 - 400$ and $350 - 600$ nm wavelength regions. OSL results for silica glasses are compared with selected FP samples, both doped and undoped	183
7.1	(a) Potential design of a field-portable fibre dosimetry test kit. (b) Po- tential design of a field-portable fibre dosimetry test kit with integrated stimulation laser and 'lens-filter'. (c) Field-portable OSL test rig without free space optics, where all elements are fibre coupled	106
A.1	Loss of LWQ silica optical fibres with wagon wheel microstructured ge-	190
1.0	Sometry.	220
A.2	Electron mean free path and range in fluoride phosphate glass.	221
A.3	Electron mean free paths in fluoride phosphate glass	221
A.4	Electron Stopping Powers in fluoride phosphate glass.	222
A.5	Electron Cross Sections in fluoride phosphate glass	222
A.6	Photon mass attenuation coefficients in fluoride phosphate glass	223
A.7	Photon Mean Free Paths in fluoride phosphate glass	223
A.8	Photoelectric cross-section ceiling in fluoride phosphate glass	224
A.9	Rayleigh cross-section ceiling in fluoride phosphate glass	224
A.10	Photon Cross Sections in fluoride phosphate glass	225
B.1	Schematic diagram of a Risø DA-20 TL/OSL Reader, showing both the	
	irradiation and luminescence detection functions.	228
B.2	Glass melting facilities. Top: nitrogen atmosphere glovebox for batching	
	and melting of fluoride glasses. Bottom: open air melting and annealing	
	furnaces	229
B.3	Crucibles and glass moulds used for remelting and doping of FP glasses.	
	Vitreous carbon crucibles are used for reducing environment melts; the	
	platinum crucible is used for open air, oxidising environment melts.	
	Brass moulds are polished before use.	230
B.4	Soft glass extrusion machine, used for all extrusions of fluoride phosphate	
	preforms. The inside of the body is shown by a cross section diagram in	
	Section 4.2, Figure 4.1	231
B.5	Soft glass optical fibre draw tower.	233
D 1		
D.1	Comparison of stopping power values for electrons in water, calculated	0.00
ЪA	using FENELOFE and ESTAR.	230
D.2	Comparison of stopping power values for electrons in aluminium, calcu-	007
	lated using PENELOPE and ESTAR	237

- D.4 Simulated energy of transmitted primary particles from a 2.28 MeV electron beam (left) and a 100 keV photon beam (right) by layers of FP glass with varying thickness. Simulation was performed using PENELOPE. 238

List of Tables

1.1	$^{90}\mathrm{Sr}/^{90}\mathrm{Y}$ Radiation Sources Used for Optical Fibre OSL Experiments	20
1.2	Comparison of specifications for an EMI 9235 QB photomultiplier tube	
	and two SPADs, a Laser components $\operatorname{COUNT}(\widehat{\mathbbm R})\text{-}\operatorname{Blue}$ and a Micro Pho-	
	ton Devices PDM	26
2.1	Representative selection of fluoride phosphate glass samples analysed for	
	their luminescence behavior	33
2.2	Composition of several fluoride phosphate glasses as determined by anal-	
	ysis with an electron microprobe	35
2.3	ICPMS/OES analysis of fluoride phosphate glass samples. The concen-	
	tration, c (ppm), of impurity ions is shown	37
2.4	Effect of glass fabrication atmosphere on the OSL response of fluoride	
	phosphate glasses	41
2.5	Activation Energy (E) , Frequency Factor (s) and Lifetimes at T = 293	
	K (τ) for FP1 glass using initial rise data	45
3.1	Representative selection of doped fluoride phosphate glass samples. At-	
	mosphere refers to the conditions in which the glass was melted: the	
	label 'ox' corresponds to an ambient atmosphere containing oxygen; the	
	'red' label corresponds to a controlled glovebox atmosphere purged with	
	nitrogen, creating reducing conditions.	63
3.2	Activation energy (E), frequency factor (s) and lifetimes at $T = 293$ K	
	(τ) of sample Mn-ox.	73
3.3	Activation energy (E), frequency factor (s) and lifetimes at $T = 293$ K	
	(τ) of sample Tb-red	78
3.4	OSL response of doped and undoped FP1 glass, fabricated under both	
	oxidising and reducing conditions, integrated from 0 - 0.2 s. $275 - 400$	
	nm indicates OSL in this wavelength region, achieved using a HOYA	
	U340 filter and 470 nm stimulation. $350 - 600$ nm indicates emission in	
	this wavelength region achieved with a Schott BG39 filter and 870 nm	
	0 0	

4.1	Summary of solutions trialled for etching of fluoride phosphate glass $\ . \ .$	98
5.1	Composition of FP1 glass, the molecular weight and stopping power of each element is listed along with the atomic percentage of the element	
5.2	in the material	117
	Measurements were performed using both wavelength regimes: stimula-	
	tion at 532 nm using a Schott BG3-BG39 filter stack and stimulation at	147
		141
6.1	Silica glass samples analysed in this chapter.	161
6.2	OSL response of LWQ and F300 silica glasses, taken for both wavelength $% \mathcal{A}$	
	regions using either a HOYA U340 filter or a Schott BG39. Beta irradi-	
	ation applied for 10 s, and OSL intensities are normalised for mass	162
6.3	Activation Energy (E) , Frequency Factor (s) and Lifetimes at T = 293	
	K (τ) for LWQ silica using initial rise data	168
6.4	Activation Energy (E) , Frequency Factor (s) and Lifetimes at T = 293	
	K (τ) for MCVD1 silica using initial rise data	168
6.5	Activation Energy (E) , Frequency Factor (s) and Lifetimes at T = 293	
	K (τ) for MCVD2 silica using initial rise data	169
6.6	Length of silica fibre at which an OSL signal is measurable using an ab-	
	sorbed dose of 15.5 ± 0.5 Gy from a ${}^{90}\text{Sr}/{}^{90}\text{Y}$ beta source. Measurements	
	were performed using both wavelength regimes: stimulation at 532 nm	
	using a Schott BG3-BG39 filter stack, and stimulation at 852 nm using	1 - 1
0.7	a Schott BG39 filter.	171
0.7	OSL response of silica glasses compared with doped and undoped FP1	
	glass, fabricated under both oxidising and reducing conditions, inte-	
	grated from 0 - 0.2 s. 275 - 400 nm indicates OSL in this wavelength	
	fegion, achieved using a HOTA 0.540 inter and 470 init stimulation. 550	
	Schott BG39 filter and 870 nm stimulation.	183
A.1	Example of purity of commercial silica glasses. Data taken from Heraeus	
	Quarzglass.	219